審 査 の 結 果 の 要 旨

氏　　名　　黄　立中

Tooth-shaped plasmonic multilayer structures for light emission and SERS detection

（SERS 検出と光放出のための歯状多層膜プラズモン構造体）

PhD thesis defended by Li-Chung HUANG

Plasmonic nanostructures have been used in a wide range of applications covering bio-sensing and light energy conversion. Plasmonic resonances are used to confine light on single nanostructures (e.g., nanoparticles) which are randomly dispersed on a substrate or in a solution. Recent progress in micro-nano fabrication techniques (i.e., electron beam lithography) has made it possible to obtain ensemble of well-ordered nanostructures on substrates. Particularly, formation of gaps between subwavelength structures presents many advantages for applications. Plasmonic gap resonances have been found to efficiently confine light in the gaps which can be functionalized to perform molecular detection. Although these plasmonic structures have been used to examine light confinement mechanism and report high sensitivity in surface enhanced Raman spectroscopy (SERS), practical applications are impeded by the fabrication cost involved with the required precise control of the separation of the plasmonic nanostructures obtained by electron beam lithography. Huang proposes to control the separation of plasmonic structures using multilayer thin films consisting of stacks of alternating metal and dielectric thin films and a subsequent selective etching of the dielectric thin film to form arrays of nanogap cavities which sustain plasmonic standing waves.

The manuscript consists of five chapters.

Chapter One introduces surface plasmons and their ability to concentrate light in nanogaps. Properties of plasmons resonances are categorized into propagating, localized and standing wave plasmons. Structures having arrays of nanogap cavities are presented and their ability to concentrate light in the nanocavities illustrated by simulation for the different types of plasmonic resonances. The possibility to apply standing wave plasmons to SERS substrates is introduced.

Chapter Two discusses the possible fabrication techniques for the proposed array of nanogap cavities. It is first recognized that nanogaps of small size in the range of 10 nm are best obtained by bottom-up techniques. However the bottom-up techniques have reproducibility issues. Huang proposes to apply thin film technology to obtain a well-defined multilayer structure (with feature size down 10 nm) that is used to produce nanogaps in the cross-section of the multilayer. Multilayer thin films consisting of stacks of alternating metal and dielectric thin films are fabricated with accurate thicknesses using thin film technology on flat substrates. The planar structure of the multilayer offers no plasmonic resonances to excite. Huang uses cross-sections of the multilayer structure to excite plasmonic resonances. Two configurations are presented, namely, cross-sections obtained by cleaving the substrate (multilayer cross-section sample) and cross-sections obtained by etching periodic trenches in the multilayer (array of multilayer trenches). The cross-sections offer well separated plasmonic subwavelength structures due to the separation of the metal layer by a dielectric layer, which thickness can be accurately fabricated as thin as 10 nm. Finally, the multilayer consisting of a stack of a metal/dielectric layers can be selectively etched, so that the dielectric material is removed and air gaps (nanocavities) sustaining standing waves are released. The cross-sections resemble tooth arrangement, so that the studied structure was named “tooth-shaped plasmonic structure”.

In Chapter Three, the near field and far field properties of the two proposed structures (multilayer cross-section and array of multilayer trenches) are presented, and the structures are optimized to sustain plasmonic standing wave resonances at specific wavelengths (closed to the wavelengths of the available lasers used in SERS). The advantages of the structures’ nanogaps sustaining plasmonic standing waves are discussed. The resonance wavelength of the structures can be controlled over a wide range of wavelengths by varying the length of the air gap nanocavities for the cross-section structure. For the array of multilayer trench structure, the excitation of the plasmonic resonance is only weakly dependent on the incident angle of light and, therefore, this structure facilitates alignment and increases light collection in the structure. The designed structures are fabricated by depositing Ag/Si thin film multilayers on a single crystal substrate. The multilayer cross-section structure is obtained by cleaving the substrate and polishing the cross-section. The array of multilayer trench structure is obtained by etching a line-and-space resist pattern fabricated on the multilayer. Subsequent selective etching of silicon is performed to form the air nanogaps. Surface enhanced Raman response of the fabricated structure is recorded using thiophenol as the target molecule. The etching depth of the dielectric layer made of silicon is estimated by measuring the resonance shift for different etching times and relating the shift to the etching depth using simulation. A correlation between the etching time of the silicon and the intensity of the Raman signal was found, providing evidence for the formation of standing wave plasmons in the air nanocavities.

In Chapter Four, the array of multilayer trenches without the etching fabrication step is used as a tunable infrared emitter. The planar structure forming a multilayer grating array is obtained by etching a line-and-space resist pattern fabricated on the multilayer. As a result of the multi gap structure sustaining standing waves, very high and selective light absorption can be obtained for the desired wavelength in the infrared region. The spectrally selective light absorption of the structure is characterized by measuring the reflectance of the sample and compared with simulated reflectance. The reflectance dip of the plasmonic resonance corresponding to light absorption is observed. The weak dependency of the resonance on the incident angle of light is explained and confirmed experimentally. The tunable absorption peak in the infra-red region can be used to obtain a tunable infrared light source. By heating the structure, an emission peak of polarized infrared light is observed and characterized in terms of emittance.

In summary, HUANG proposes an original approach to fabricate arrays of nanogaps with feature size down to 10 nm for surface enhanced Raman scattering detection. Selective etching of the dielectric materials forming a well-defined multilayer structure of alternating metal and dielectric thin films is used to fabricate nanocavity arrays on the multilayer cross-section and trench. The nanocavity arrays offer advantages in terms of the control of the resonance wavelength and weak dependence on the incident angle of excitation light. The nanocavity array structures demonstrate strong SERS signal enhancement using reproducible fabrication techniques that are amenable to large scale fabrication, thus providing the possibility for large scale production of high-quality tunable SERS substrates.

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